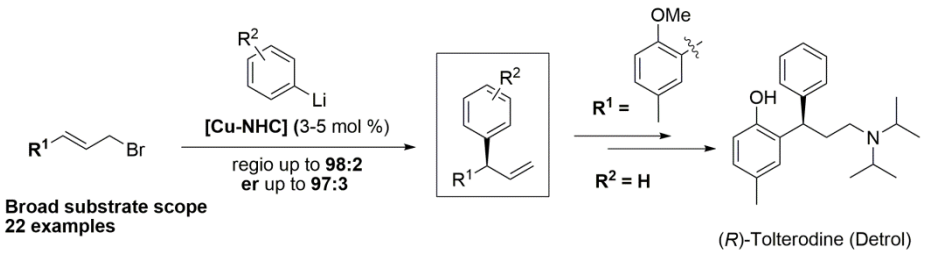
Chapter 3
Chiral Diarylmethanes via Copper-Catalyzed Asymmetric Allylic Arylation with Organolithium Compounds



A highly enantioselective copper/*N*-heterocyclic carbene (NHC) catalyzed allylic arylation (AAAr) with organolithium compounds is presented. The use of commercial or readily prepared aryllithium reagents in the reaction with allyl bromides affords a variety of chiral diarylvinylmethanes, comprising a privileged structural motif in pharmaceuticals, in high yields with good to excellent regio- and enantioselectivities. The versatility of this new transformation is illustrated in the formal synthesis of the marketed drug tolterodine (Detrol).

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3.1 Introduction

The enantioselective synthesis of diarylmethane tertiary stereogenic centers, a structural motif that is present in many natural products and pharmaceuticals, has attracted considerable attention in recent years.[1] Examples of compounds bearing this subunit include podofilox (Condylox),[1b] nomifensine, CDP-840,[1c] (+)-sertraline (Zoloft)[1d] and (*R*)-tolterodine,[1e] the latter being a drug with blockbuster status. Catalytic asymmetric synthesis methods to access these compounds comprise both stereospecific and enantioselective transformations.[2,3,4,5,6,7,10] The first approaches, based on chiral starting materials, include a nickel-catalyzed cross-coupling of 1,1-diarylethers described by the group of Jarvo[3a] and a stereoretentive rhodium-catalyzed decarbonylation of enantioenriched *β*,*β*-diarylpropionaldehydes reported by the group of Carreira.[3b] Catalytic enantioselective strategies include Friedel-Crafts reactions,[4a] iridium-catalyzed asymmetric hydrogenation of 1,1-diarylalkenes,[4b,c] a cooperative rhodium/phosphoric acid-catalyzed asymmetric arylation of *α*-aryl- *α*-diazo compounds with aniline derivates,[4d] and a copper-catalyzed enantioselective electrophilic arylation of allylic amides with diaryliodonium salts.[4e] Another attractive approach has been reported by Fu and co-workers, where racemic benzylic alcohols were converted into 1,1-diarylalkanes using an enantioselective nickel-catalyzed cross-coupling protocol.[4f]

Transition-metal-catalyzed 1,4-addition of organoboron compounds to substituted electron-deficient styrenes has also been shown to be effective in accessing this structural motif, in particular using a rhodium-based catalyst.[5] Additionally, the catalytic enantiotopic group selective cross-coupling of achiral geminal bis(pinacolboronates),[6] and the recently developed additions of malonates[7a] or boron reagents[7b,c] to quinone methides provide useful chiral *gem*-diarylmethines and boronic ester derivatives.

Diarylmethane stereogenic centers can also be accessed via metal-catalyzed arylation of aryl-substituted allyl electrophiles using organometallic reagents.[2a,8d-g] We envisioned that an asymmetric allylic arylation (AAAr) with highly reactive aryllithium reagents, as presented here, would provide a viable and attractive alternative to access these chiral structures. In the case of copper, the use of the corresponding alkyl nucleophiles has been well established, and AAA reactions of a wide range of alkyl metal reagents and allylic systems have been reported.[8a-e,9] In contrast, the introduction of less reactive aryl groups continues to provide major challenges, and several groups embarked on the development of a general and efficient catalytic system for the formation of chiral diarylmethanes based on this transformation.[10] High regio- and enantioselectivity was demonstrated by Hoveyda and co-workers using chiral bidentate *N*-heterocyclic carbenes (NHC) for the AAAr with aryldialkylaluminium reagents,[10a] derived from the corresponding organolithium compounds. Bidentate NHC have also been employed by the group of Hayashi in the allylic substitution with less reactive arylboronates and allyl phosphates.[10b,c] Additionally, aryl Grignard reagents have been employed by Tomioka and co-workers using chiral monodentate *N*-heterocyclic carbenes.[10d,e]

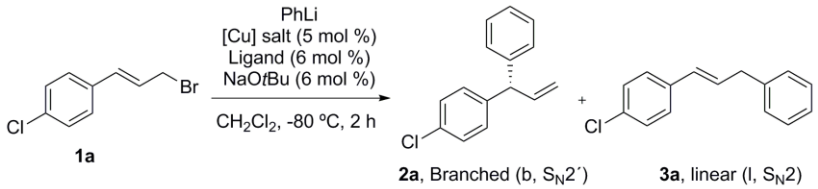
Recently, we reported that organolithium compounds, among the most widely used reagents in organic synthesis, can be directly used as nucleophiles in copper-catalyzed AAA with a variety of allyl systems.[11] The use of Taniaphos or monodentate phosphoramidites as chiral ligands in dichloromethane and *n*-hexane as solvent and co-solvent, allowed us to control the high reactivity of these compounds and obtain excellent regio- and enantioselectivities in AAA reactions. Disappointingly, the reaction with PhLi under these conditions consistently led to poor regioselectivities.[11a] As aryllithium compounds are commercially available or readily accessible by lithium–halogen exchange[12] and, moreover, they are often employed as precursors for other organometallic compounds (Al, B, Zn), the development of a general AAAr method using these reagents is highly desirable.

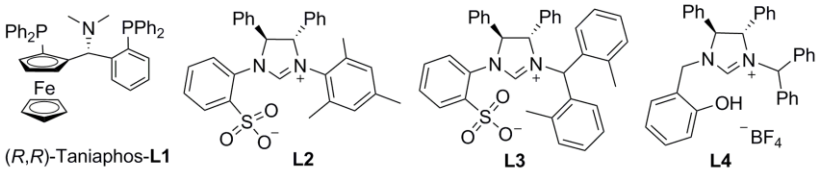
Herein, we report the first regio- and enantioselective method for the copper-catalyzed AAAr with aryllithium compounds to afford optically active diarylvinylmethanes with excellent regio- and enantioselectivities (S_N2':S_N2 up to 99:1, er up to 99:1).

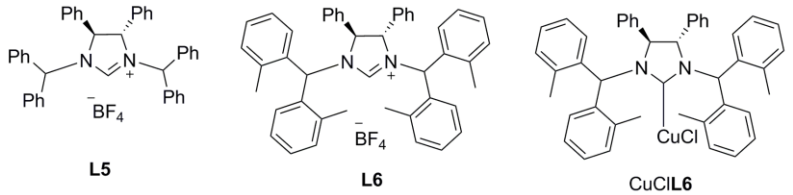
3.2 Results and discussion

The reaction between allyl bromide **1a** and commercially available PhLi, in the presence of catalytic amounts of CuBr•SMe_2 and chiral ligands, was used for the initial optimization (Table 1).[11a] PhLi was diluted with *n*-hexane and added over 2 h to a solution of allyl bromide in CH_2Cl_2 at –80 °C. As the use of chiral phosphorus ligands, which provided high selectivity for alkyllithium reagents,[11] did not lead to satisfactory results (entry 1, Table 1 and results not shown), we decided to evaluate a series of strong σ-donating NHCs. The use of chiral bidentate NHC-Cu catalysts, in situ prepared by deprotonating imidazolium salt **L2**[10a] and structurally related imidazolium salts **L3** and **L4**, led to low or moderate regioselectivities (entries 2-4, Table 1).[13] We then examined sterically demanding chiral monodentate NHC ligands, and an improved regio- and good enantioselectivity were observed when the catalyst derived from imidazolium salt **L5**[10d] was used (entry 5, Table 1). To our delight, the catalyst derived from **L6**, having *o*-tolyl moieties, led to a major increase in regioselectivity toward the branched product **2a** (b:l = 97:3) with excellent enantioselectivity (97:3 er, entry 6). A possible rationale is that the use of bulkier aryl substituents on the N atoms enhances the reductive elimination step favoring the S_N2' product.[14] Importantly, the isolated air-stable CuCl-NHC complex derived from **L6** gave the same result, avoiding the use of NaO*t*Bu and simplifying the procedure (entry 7).

Table 1. Screening of different ligands[a]





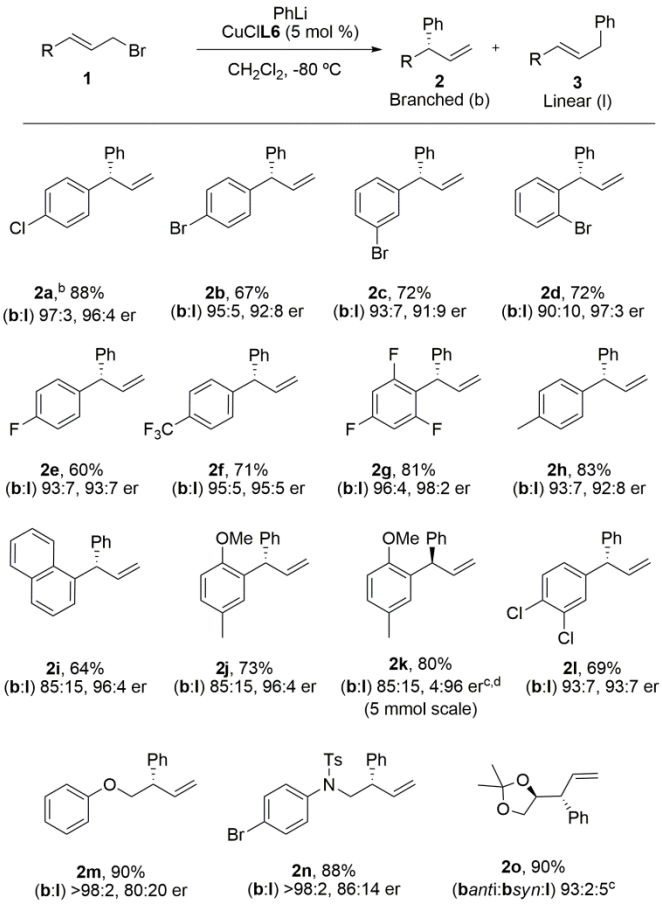


entry	L	[Cu]	**2a**:**3a**[b]	**2a**, er[c]
1	**L1**	CuBr•SMe_2	10:90	n.d.
2	**L2**	CuBr•SMe_2	70:30	n.d.
3	**L3**	CuBr•SMe_2	47:53	n.d.
4	**L4**	CuBr•SMe_2	37:63	n.d.
5	**L5**	CuBr•SMe_2	63:37	94:6
6	**L6**	CuBr•SMe_2	97:3	97:3
7	CuCl**L6**		97:3	97:3

a) Conditions: allyl bromide (0.2 mmol) in CH_2Cl_2 (2 mL). PhLi (0.3 mmol, 1.8 M solution in *n*-dibutyl ether diluted with *n*-hexane to a final concentration of 0.3 M) was added over 2 h. All reactions gave full conversion. b) **2a**/**3a** ratios and conversions determined by GC-MS and ^{1}H-NMR analysis. c) Determined by chiral HPLC after conversion to the corresponding primary alcohol using a hydroboration-oxidation procedure. (see experimental section).

Having established optimal conditions, we next investigated the substrate scope and generality of this arylation reaction by using PhLi; the results are summarized in Scheme 1.

Scheme 1. Substrate scope for the Cu-catalyzed enantioselective allylic arylation[a,e]



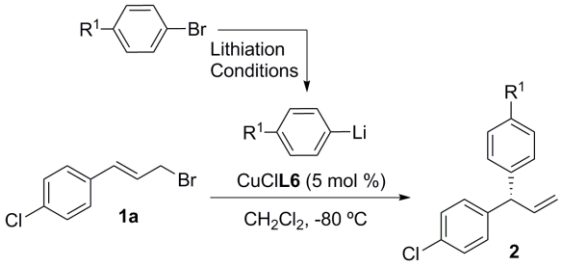
a) Conditions: allyl bromide **1** (0.2 mmol) in CH_2Cl_2 (2 mL). PhLi (0.3 mmol, 1.8 M solution in *n*-dibutyl ether diluted with *n*-hexane to a final concentration of 0.3 M) was added over 2 h. All reactions gave full conversion. **2**/**3** ratios and conversions determined by GC-MS and ^{1}H-NMR analysis. Er determined by chiral HPLC after conversion to the corresponding primary alcohol using a hydroboration-oxidation procedure (see experimental section). b) The absolute configuration of **2a** was assigned by comparing the sign of the optical rotation with the literature value (ref. 10d). c) (4*R*,5*R*)-**L6** was used instead. d) 5 mmol (1.2 g) scale reaction using 3 mol % of catalyst. e) Isolated yield of S_N2' product**.**

The presence of chloro or bromo substituents at the aromatic ring of the substrate were well tolerated, affording the corresponding diarylvinylmethanes in high yields and selectivities and providing synthetically useful functionalities for further transformations (**2a-d**). Importantly, no evidence of lithium–halogen exchange was observed, highlighting the high chemoselectivity of the reaction. Trifluoromethylated and fluorinated compounds, which are very important in the agrochemical and pharmaceutical industries,[15] were also suitable substrates furnishing the corresponding *gem*-biaryl products with excellent selectivities (2**e-g**). High selectivities were also obtained when electron-donating substituents (**1h**, **1j** and **1k**) or sterically demanding substrates such as 1-naphthyl-substituted allyl bromide (**1i**) or compounds **1j** and **1k** were used with this Cu-NHC-based catalyst system. Arylation of compound **1l** was accomplished with good regio- and enantioselectivity, providing **2l**, which is an advanced intermediate in the synthesis of sertraline,[10d] a major pharmaceutical for the treatment of depression. Compound **2k** bearing *m*-methyl and *o*-methoxy substituents at the aryl ring was also prepared with good regio- (85:15) and excellent enantioselectivity (96:4) serving as precursor for the synthesis of (*R*)-tolterodine (see below). Importantly, when this reaction was performed on a larger scale (5 mmol, 1.2 g), using a lower catalyst loading (3 mol %), product **2k** was still obtained with the same selectivities without erosion of yield. Allylic bromides bearing a phenol ether or protected amine provided highly functionalized chiral building blocks **2m** and **2n**, with excellent yields and regioselectivity although the enantioselectivity decreased slightly. The use of a dioxolane-containing allylic bromide **1o** led to the diastereoselective formation of valuable 1,2-hydroxyallyl moiety **2o** with excellent stereocontrol for the *anti*-isomer.[16]

We next explored the scope of the reaction with respect to the aryl lithium component using **1a** as the electrophilic counterpart. However, to our surprise, no conversion was observed when *p*-tolyllithium or (*p*-methoxyphenyl)lithium solutions, prepared in THF via bromide–lithium

exchange using *t*-BuLi, were employed in the reaction under previously optimized conditions (entries 1 and 2, Table 2).

Table 2. Screening of different conditions for the preparation of reactive homemade aryllithium compounds[a]



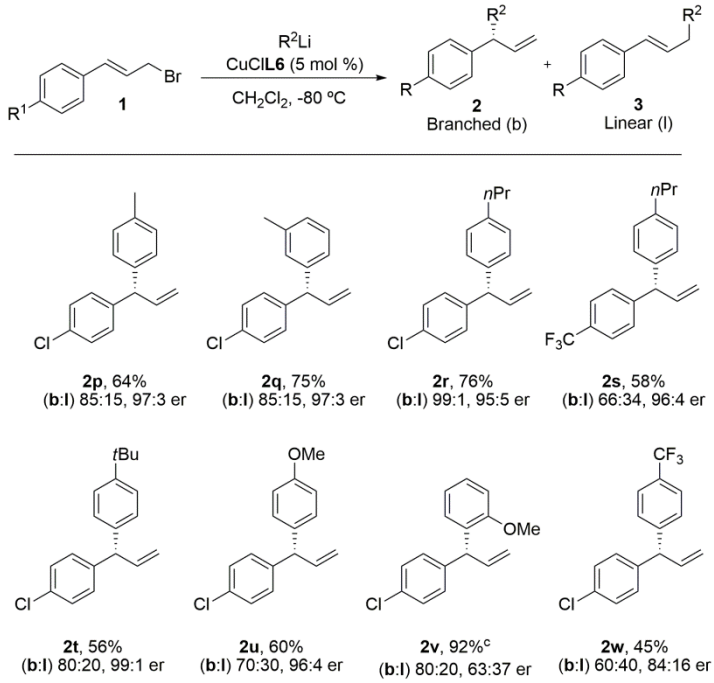
entry	R^1	lithiation conditions (final conc, M)	Conv (%)/ **2**:**3, 2a** er
1	OMe	*t*-BuLi, -30 °C to rt, 1h; 1:2 THF/Pentane (0.57)	0
2	Me	*t*-BuLi, -30 °C to rt, 1h; 1:2 THF/Pentane (0.57)	0
3	Me	*t*-BuLi, -30 °C to rt, 1h; 1:2 Et_2O/Pentane (0.57)	0
4	Me	Li, Et_2O, rt, 2h (1.5)	0
5[b]	Me	Li, Et_2O, rt, 2h (1.5)	47/95:5
6	Me	*n*-BuLi, -30 °C to rt, 1h; 4:3 Et_2O/Hexane (0.69)	>99/85:15, **2a** 97:3

a) Conditions: allyl bromide (0.2 mmol) in CH_2Cl_2 (2 mL). RLi (0.4 mmol) was diluted with *n*-hexane to a final concentration of 0.4 M and was added over 2 h. **2a**/**3a** ratios and conversions determined by GC-MS and ^{1}H- NMR analysis. Er determined by chiral HPLC after conversion to the corresponding primary alcohol using a hydroboration-oxidation procedure (see experimental section). b) 1-chloro-4-methylbenzene was used instead.

Changing THF to less coordinating Et_2O as solvent led to the same result (entry 3, Table 2). As the use of *t*-BuLi to effect lithium-halogen exchange generates one equivalent of 2-methylpropene, which may coordinatively interfere with the Cu catalyst, we decided to use a different method for the lithiation. Lithium metal[17] in combination with *p*-bromotoluene was still unsatisfactory, although the use of *p*-chlorotoluene allowed us to reach 47% conversion in the corresponding AAAr reaction (entry 5). Finally, we found that the use of *n*-BuLi and

Et_2O as solvent, which avoids S_N2 reaction[18] of the resulting ArLi and *n*-BuBr, allowed us to obtain the desired product with full conversion and high regio- and enantioselectivity (entry 6, table 3 and **2p**, Scheme 2). Under these conditions, aryllithium bearing electron-donating methoxy- and alkyl groups as well as electron-withdrawing -CF_3 substituents participate in the reactions with allyl bromides **1a** and **1f** in good to excellent yields and regio- and enantioselectivities (Scheme 2). A limitation found for this Cu-NHC based catalytic system is that the use of *o*-methoxy substituted phenyllithium suffered from diminished enantioselectivity as seen for compound **2v**.

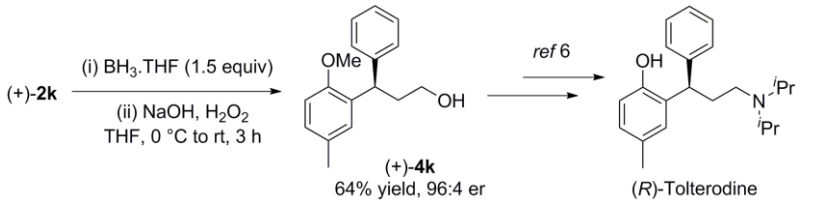
Scheme 2. Scope of aryllithium compounds[a,b]



a) Conditions: allyl bromide (0.2 mmol) in CH_2Cl_2 (2 mL). R^2Li (0.4 mmol) was diluted with *n*-hexane to a final concentration of 0.4 M and was added over 2 h. All reactions gave full conversion. **2**/**3** ratios and conversions determined by GC-MS and ^{1}H-NMR spectroscopy. Er determined by chiral HPLC after conversion to the corresponding primary alcohol using a hydroboration-oxidation procedure (see experimental section). b) Isolated yield of S_N2' product. c) Isolated a 80:20 mixture of S_N2': S_N2 product.

To finally demonstrate the efficiency and applicability of the present methodology, we performed the synthesis of chiral alcohol **4k**,[6] a precursor of (*R*)-tolterodine (Detrol). Here the catalytic allylic arylation of **2k** with phenyllithium is followed by a one-pot hydroboration-oxidation to afford advanced intermediate **4k** in 64% yield (96:4 er) (Scheme 3). (*R*)-Tolterodine is a potent competitive muscarine receptor antagonist for the treatment of urinary incontinence and cystitis.[1e]

Scheme 3. Conversion of (*R*)-2k into (*R*)-4k, a synthetic intermediate of tolterodine (Detrol).



3.3 Conclusions

In summary, the highly enantioselective Cu-catalyzed direct allylic arylation using organolithium compounds has been described. The use of readily available aryllithium reagents in combination with allylic bromides and use of a copper-NHC catalyst are key factors for the success of this reaction. The only stoichiometric waste produced in this novel transformation is LiBr. The use of *n*-BuLi was found essential for the preparation of aryllithium compounds. The broad substrate and reagent scope and the application of the new method in the formal catalytic enantioselective synthesis of (*R*)-tolterodine (Detrol) illustrates the potential of this allylic arylation for the synthesis of important chiral diarylmethane structures.

3.4 Experimental section

3.4.1 General procedures

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890: MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). ^{1}H- and ^{13}C-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) or a Varian VXR300 (300 and 75 MHz, respectively) using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H, δ 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Optical rotations were measured on a *Schmidt + Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Enantiomeric ratios were determined by HPLC analysis using a Shimadzu LC-10AD*VP* HPLC equipped with a Shimadzu SPD-M10A*VP* diode array detector.

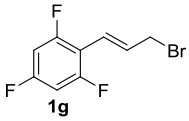
All reactions were carried out under nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. Dichloromethane, diethyl ether, tetrahydrofuran and toluene were used from the solvent purification system (MBRAUN SPS systems, MB-SPS-800). *n*-Hexane was dried and distilled over sodium. All copper-salts ($CuBr{\bullet}SMe_2$, CuCl), (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine, (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine, (*R*,*R*)-taniaphos (**L1**), $Pd(OAc)_2$, (±)-BINAP, mesityl bromide, NaO*t*Bu, anhydrous acetonitrile, PhLi (1.8 M in *n*-Bu_2O), *o*-tolylmagnesium bromide (2.0 M in Et_2O), vinylmagnesium bromide (1.0 M in THF), *n*-BuLi (1.6 M in *n*-hexane), $BH_3{\bullet}$THF (1.0 M in THF) were purchased from Aldrich, and used without further

purification. Ligands **L2**[19], **L5**, **L6** and **CuClL6**[10d,e] were prepared from the corresponding chiral diamines following the indicated procedures described in the literature (see below).

Racemic products were synthesized by reaction of the allyl bromides with the corresponding organolithium reagent at -78 °C in dichloromethane in the presence of racemic **CuClL6** (5 mol %).

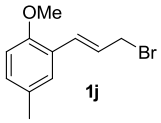
3.4.2 Preparation of allyl bromides

All the allyl bromides were synthesized from the corresponding aldehydes in two-steps *via* 1,2-addition with a vinyl magnesium bromide/PBr_3 bromination sequence, using literature procedures.[20] Physical data of compounds **1a**[20], **1b**, **1c**, **1d**[21], **1e**[22], **1f**[20a,21], **1h**[23], **1i**[20a], **1k**[24], **1l**, **1m**[25], **1n**[26] match with the reported data. 2-Methoxy-5-methylbenzaldehyde, precursor of allyl bromide **1j**, was prepared *via* methylation of the corresponding phenol using a procedure reported in the literature.[27] Physical data of compounds that have not been previously reported are presented below.



1g

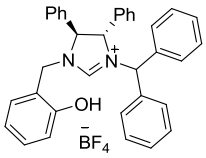
(*E*)-2-(3-bromoprop-1-enyl)-1,3,5-trifluorobenzene (1g): Obtained **1g** (461 mg, yield = 93%) as a pale yellow low melting solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.44 (m, 4H), 4.13 (d, J = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 162.4, 160.4, 159.8, 131.5, 119.8, 109.9, 101.3, 99.5, 33.3; ^{19}F NMR (400 MHz, $CDCl_3$) δ -107.90 (p, J = 8.0 Hz, 1F), -109.28 – -109.72 (m, 2F); GC-MS (EI+, *m/z*): $[M+H-Br]^+$: 172.
Note: HMRS using electrospray does not provide the required mass.



1j

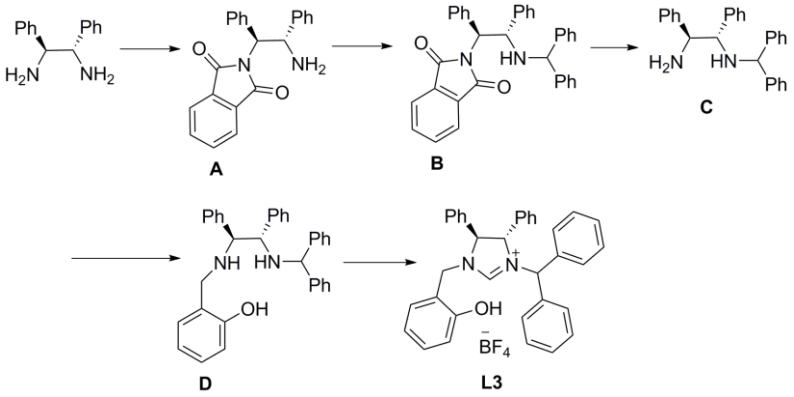
(*E*)-2-(3-bromoprop-1-enyl)-1-methoxy-4-methylbenzene (1j): Obtained **1j** (804 mg, yield = 90%) as a greenish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J = 7.0, 2.2 Hz, 1H), 7.12 – 7.01 (m, 1H), 6.95 (d, J = 15.6 Hz, 1H), 6.77 (dd, J = 8.4, 4.4 Hz, 1H), 6.42 (dt, J = 15.7, 7.9 Hz, 1H), 4.19 (dd, J = 7.8, 1.0 Hz, 2H), 3.82 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 134.9, 131.5, 130.3, 128.7, 114.7, 56.1, 31.5, 20.8; HRMS (APCI+, *m/z*): calculated for $C_{11}H_{13}O$ $[M\text{-}HBr]^+$: 161.0961, found: 161.0962.

3.4.3 Procedure for the synthesis of chiral imidazolium salts



L3

(–)-(4*S*,5*S*)-3-benzhydryl-1-(2-hydroxybenzyl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (L3):



Molecular sieves 4Å (2 g), (1*S*,2*S*)-(-)-1,2-diphenylethylenediamine (220 mg, 1.1 mmol, 1 equiv) and phthalic anhydride (154 mg, 1.1 mmol, 1 equiv) were added to a solution of *p*-TsOH•H_2O (197 mg, 1.1 mmol, 1

equiv) in toluene (10 mL). The mixture was heated to reflux and stirred overnight. The resulting mixture was filtered through celite with CH_2Cl_2 (10 mL). The resulting solution was stirred overnight with saturated aqueous K_2CO_3 (10 mL). The organic phase was separated, dried over $MgSO_4$, filtered and the solvent evaporated to give compound **A** (285 mg, 81% yield) as a white solid.[28]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.98 (m, 1H), 7.95 – 7.84 (m, 1H), 7.81 – 7.67 (m, 2H), 7.37 (dddd, J = 12.5, 10.6, 5.5, 3.5 Hz, 6H), 7.30 – 7.24 (m, 4H), 5.63 (d, J = 5.6 Hz, 1H), 5.08 (d, J = 5.6 Hz, 1H).

To a solution of **A** (285 mg, 0.84 mmol, 1 equiv) in CH_3CN (15 mL), K_2CO_3, (303 mg, 2.2 mmol, 2.6 equiv) and bromodiphenylmethane (650 mg, 2.6 mmol, 3.1 equiv) were added and the resulting mixture was stirred while heated at reflux for 6 h. The mixture was then cooled to room temperature, concentrated *in vacuo* and the residue was diluted with CH_2Cl_2 (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (20%, Et_2O/Pentane) to afford the compound **B** (335 mg, 75% yield) as a white solid.[28]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.4, 3.1 Hz, 2H), 7.75 (dd, J = 5.5, 3.0 Hz, 2H), 7.44 – 7.30 (m, 3H), 7.21 (d, J = 6.7 Hz, 7H), 7.16 – 7.04 (m, 11H), 5.60 (d, J = 11.0 Hz, 1H), 4.83 (d, J = 11.0 Hz, 1H), 4.55 (s, 1H).

A solution of **B** (280 mg, 0.55 mmol, 1 equiv) and hydrazine monohydrate (2.0 mL, 50 mmol, 91 equiv) in ethanol (10 mL) was stirred at reflux for 4 h. The mixture was then cooled to room temperature and concentrated *in vacuo*. The residue was diluted with CH_2Cl_2 (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The

combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (50%, EtOAc/Pentane) to afford compound **C** (146 mg, 70% yield) as a pale yellow amorphous solid.[28]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 6.22 (m, 20H), 4.57 (s, 1H), 4.11 (d, J = 7.1 Hz, 1H), 3.69 (d, J = 7.1 Hz, 1H), 3.09 (s, 3H).

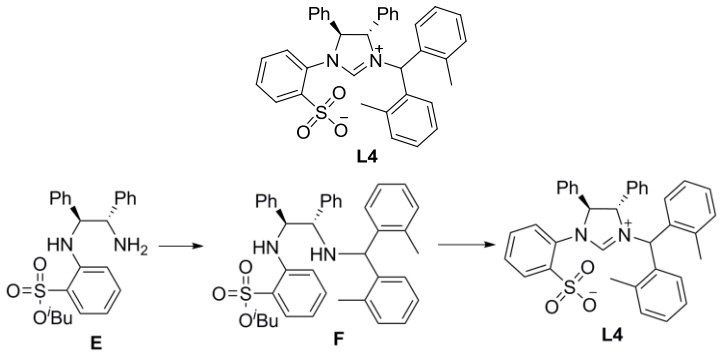
Salicylaldehyde (54 μL, 0.5 mmol, 1.1 equiv) was added dropwise to a solution of **C** (170 mg, 0.45 mmol, 1 equiv) in dry CH_3CN (5 ml) containing activated molecular sieves 4Å (1 g). After stirring the mixture for 6h, $NaBH_3CN$ (34 mg, 0.54 mmol) and AcOH (0.2 ml) were added and the mixture was stirred overnight. A saturated solution of $NaHCO_3$ (5 ml) was then added and the mixture was stirred for 15 min. The mixture was diluted with water (10 mL), the layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3×5 ml) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (10%, EtOAc/Pentane) to afford compound **D** (130 mg, 60% yield) as a pale yellow amorphous solid.[29]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.09 (m, 17H), 7.09 – 6.99 (m, 2H), 6.93 (d, J = 7.6 Hz, 4H), 6.78 (t, J = 7.4 Hz, 1H), 5.42 (s, 3H), 4.60 (d, J = 3.0 Hz, 1H), 3.94 – 3.73 (m, 3H), 3.67 (d, J = 13.6 Hz, 1H).

In a flame-dried flask, diamine **D** (130 mg, 0.27 mmol, 1 equiv), NH_4BF_4 (90 mg, 0.81 mmol, 3 equiv), toluene (3 mL) and $CH(OMe)_3$ (3 mL) were added and the mixture was heated to reflux for 16 h. The solvents were removed and the crude oil was triturated in Et_2O to afford a pale yellow precipitate. The solid was filtered, washed three times with Et_2O and dried under vacuum to yield **L3** (25 mg, 20% yield). Due to hygroscopic properties **L3** has to be kept under inert atmosphere.[29] $[\alpha]_D^{20}$ = –114.0 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.56 – 7.30 (m, 15H), 7.30 – 7.17 (m, 5H), 7.03 – 6.88 (m, 3H), 6.80 (t, J

= 7.4 Hz, 1H), 6.73 (dd, *J* = 7.4, 1.7 Hz, 1H), 5.28 (s, 1H), 5.19 (d, *J* = 14.7 Hz, 1H), 4.77 – 4.54 (m, 2H), 4.10 (d, *J* = 14.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 157.9, 135.0, 134.8, 134.4, 133.9, 131.4, 131.0, 130.4, 130.0, 129.9, 129.8, 129.7, 129.6, 129.4, 129.1, 127.6, 127.5, 127.3, 121.0, 120.1, 110.9, 73.2, 72.2, 64.6, 55.4, 47.9; ^{19}F NMR (400 MHz, $CDCl_3$) δ -151.7, -151.8; HRMS (ESI+, *m/z*): calculated for $C_{35}H_{31}N_2O$ $[M+H]^+$: 495.2431, found: 495.2414.

(–)-2-((4*S*,5*S*)-3-(dio-tolylmethyl)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium-1-yl)benzenesulfonate (**L4**):



Compound **E** was prepared according to reported literature procedure in 60% yield as a yellow solid. All physical data match with data reported.[19]

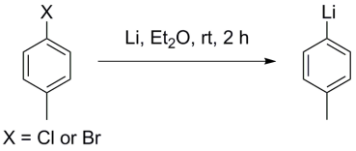
K_2CO_3 (230 mg, 1.62 mmol, 2 equiv) and 2,2'-(bromomethylene)bis(methylbenzene) (340 mg, 1.22 mmol, 1.5 equiv) were added to a solution of compound **E** (342 mg, 0.81 mmol, 1 equiv) in CH_3CN (15 mL) at room temperature. The resulting mixture was stirred at reflux for 6 h, cooled to room temperature and concentrated in vacuo. The residue was diluted with CH_2Cl_2 (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (10%, Et_2O/Pentane) to afford the compound **F** (312 mg, 63% yield) as a pale yellow solid.[28]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 8.0, 1.6 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.48 (d, J = 5.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.24 – 6.99 (m, 13H), 6.64 (t, J = 7.5 Hz, 1H), 6.45 (d, J = 8.5 Hz, 1H), 4.93 (s, 1H), 4.66 (t, J = 6.3 Hz, 1H), 3.94 (d, J = 7.0 Hz, 1H), 3.88 – 3.75 (m, 2H), 2.18 (s, 3H), 1.99 (hept, J = 6.7 Hz, 1H), 1.79 (s, 3H), 0.97 (d, J = 6.7 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 140.5, 140.2, 140.0, 139.1, 136.4, 136.3, 135.0, 130.8, 130.5, 130.4, 128.6, 128.5, 128.3, 128.2, 127.9, 127.4, 127.3, 127.1, 126.9, 126.6, 126.2, 126.1, 117.3, 115.6, 113.9, 76.3, 66.1, 62.8, 55.3, 28.1, 19.2, 19.1, 18.9, 18.8.

Diamine **F** (312 mg, 0.51 mmol, 1 equiv) was weighed out into a screw cap vial, which was sealed with a septum and purged with N_2. Acetic acid (450 μL, 15.4 mmol, 30 equiv) followed by formaldehyde (37% (aq), 196 μL, 5.15 mmol, 10 equiv) were added through a syringe. The vial was sealed with a screw cap and the mixture was allowed to stir at 110 ^{0}C (the white heterogeneous mixture becomes yellow and homogeneous upon heating). After 3 h, the mixture was allowed to cool to room temperature and diluted with Et_2O (5 mL) and water (5 mL). The reaction mixture was neutralized by the slow addition of K_2CO_3, until gas evolution ceased. CH_2Cl_2 (10 mL) was added and the aqueous layer separated. The aqueous layer was extracted further with CH_2Cl_2 (2 × 10 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford a yellow solid. The yellow solid was purified by silica gel column chromatography (3% MeOH/CH_2Cl_2) to afford imidazolium salt **L4** (200 mg, 70% yield) as a pale yellow solid.[19] $[\alpha]_D^{20}$ = –197.8 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.10 (dd, J = 7.8, 1.5 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.5 Hz, 3H), 7.48 – 7.39 (m, 5H), 7.35 (t, J = 7.5 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.23 – 7.11 (m, 4H), 7.07 – 7.01 (m, 2H), 6.95 (td, J = 7.7, 1.5 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 6.43 (d, J = 11.8 Hz, 1H), 5.67 (s, 1H), 5.19 (d, J = 11.8 Hz, 1H), 2.38 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 143.4, 138.7, 136.2, 134.6, 132.3, 132.1, 131.8, 131.7, 130.8, 130.7, 130.5, 130.0, 129.9, 129.8,

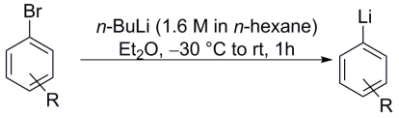
129.7, 129.6, 129.5, 129.4, 129.2, 128.9, 128.8, 127.1, 127.0, 126.9, 126.8, 75.6, 73.5, 57.8, 19.3, 18.5; HRMS (ESI-, *m/z*): calculated for $C_{36}H_{31}N_2O_3S$ $[M\text{-}H]^-$: 571.2050, found: 571.2049.

3.4.4 General procedure for the preparation of ArLi using lithium metal



The corresponding 4-halotoluene (10 mmol, 1 equiv) in anhydrous diethyl ether (6.6 mL) was added over 15 min to stirred lithium spherules (22 mmol, 2.2 equiv) at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 2 h, delivering the corresponding *p*-tolyllithium (1.5 M solution in Et_2O).[30]

3.4.5 General procedure for the preparation of ArLi using *n*-BuLi



In a flame-dried Schlenk flask equipped with septum and stirring bar, the corresponding ArBr (6 mmol, 1 equiv) in anhydrous diethyl ether (5 mL) was cooled to –30 °C and then *n*-BuLi (1.6 M in *n*-hexane, 3.75 mL, 6 mmol, 1 equiv) was added dropwise over 5 min. After complete addition, the reaction mixture was slowly warmed to room temperature and stirred for additional 1 h, delivering the corresponding ArLi (0.69 M solution in 4:3 Et_2O/*n*-hexane).[31]

Note: Due to the poor reactivity of 1-bromo-4-propylbenzene the mixture was stirred 14 h at room temperature.

3.4.6 General procedure for the copper-catalyzed asymmetric allylic arylation with organolithium reagents

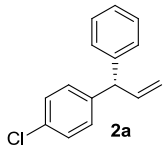
A flame-dried 10 mL Schlenk tube equipped with septum and stirring bar was charged with **CuClL6** (7.5 mg, 0.01 mmol, 5 mol %), and the substrate 0.2 mmol (if it is a solid). The tube was evacuated and filled with nitrogen. This cycle was repeated three times and then dry CH_2Cl_2 (2 mL) was added. Liquid starting materials were dissolved in dry CH_2Cl_2 (2 mL), added to the catalyst and the resulting solution was stirred under nitrogen at room temperature for 5 min. The solution was cooled down to –80 °C. In a separate Schlenk tube, the corresponding aryllithium (1.5 equiv) was diluted with dry *n*-hexane (combined volume of 1 mL) under nitrogen atmosphere and added dropwise to the reaction mixture over 2 h using a syringe pump. The flow of inert gas was turned off during the addition to prevent the organolithium drops to dry on the tip of the needle. Once the addition was complete, the mixture was stirred for another 30 min at –80 °C. The reaction mixture was quenched with a saturated aqueous NH_4Cl solution (2 mL), the mixture was warmed up to rt, diluted with diethyl ether and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 5 mL) and the combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated *in vacuo*. The crude product was submitted for the further purification and analysis.

3.4.7 General procedure for the hydroboration-oxidation of the corresponding alkenes

BH_3•THF (1.0 eq, 1.0 M solution in THF, 0.2 mmol, 1 equiv) was added to a solution of the corresponding mixture of alkenes (0.2 mmol, 1 equiv) in THF (2.0 mL) at 0 °C. The mixture was stirred for 10 min at 0 °C and for 1 h at room temperature. 15% NaOH (aq) (1.5 equiv) and 30% H_2O_2 (aq) (2 equiv) were successively added at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated NaCl (aq) and the mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under

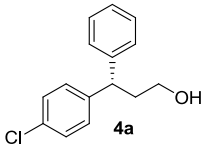
vacuum. The residue was purified by column chromatography on silica gel using a mixtures of EtOAc/pentane to afford the corresponding terminal alcohol.[10b]

3.4.8 Characterization and analysis of the molecules



2a

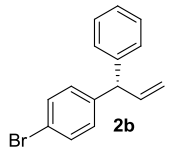
(–)-(*S*)-1-chloro-4-(1-phenylallyl)benzene (2a): Purification by flash column chromatography (SiO_2, pentane) afforded only S_N2' product **2a** (41 mg, yield = 88%) as a colorless oil.[32] 96:4 er, $[\alpha]_D^{20}$ = –9.0 (c = 1 in $CHCl_3$); [lit.[10b] (93% ee): $[\alpha]_D^{20}$ = –8.7 (c = 1.51 in $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 5H), 7.20 – 7.15 (m, 2H), 7.15 – 7.10 (m, 2H), 6.27 (ddd, *J* = 17.1, 10.2, 7.1 Hz, 1H), 5.25 (dt, *J* = 10.2, 1.4 Hz, 1H), 4.99 (dt, *J* = 17.1, 1.5 Hz, 1H), 4.71 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 141.8, 140.1, 132.2, 130.0, 128.5, 126.6, 116.8, 54.3. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



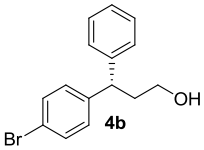
4a

(+)-(*S*)-3-(4-chlorophenyl)-3-phenylpropan-1-ol (4a): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4a** (40 mg, yield = 83%) as a colorless oil. 96:4 er, $[\alpha]_D^{20}$ = +3.5 (c = 1 in $CHCl_3$); [lit.[10b] (93% ee): $[\alpha]_D^{20}$ = +6.1 (c = 0.65 in $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 6.26 (m, 9H), 4.12 (t, *J* = 7.7 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.29 (dtd, *J* = 7.8, 6.4, 3.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.0, 132.0, 129.2, 128.7, 128.6, 127.8, 126.5, 60.9, 46.6, 37.9; HRMS (APCI-, *m/z*): calculated for $C_{15}H_{14}ClO$ $[M-H]^-$: 245.0728, found: 245.0731. Enantiomeric excess was determined by

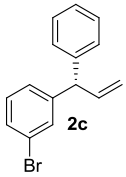
chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 90:10, 40 °C, 205 nm, retention times (min): 9.84 (minor) and 11.22 (major).



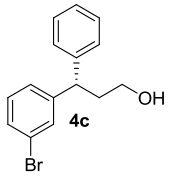
(–)-(*S*)-1-bromo-4-(1-phenylallyl)benzene (2b): Purification by flash column chromatography (SiO_2, pentane) afforded a mixture of S_N2':S_N2 (99:1) **2b** (38 mg, yield = 67%) as a colorless oil.[32] 92:8 er, $[\alpha]_D^{20}$ = –5.3 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.21 (m, 1H), 7.20 – 7.14 (m, 2H), 7.12 – 7.01 (m, 2H), 6.27 (ddd, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.25 (dt, *J* = 10.2, 1.4 Hz, 1H), 5.00 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.70 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 142.3, 141.2, 140.0, 131.5, 130.4, 128.8, 128.5, 128.5, 127.3, 127.2, 126.6, 120.3, 116.8, 54.3; HRMS (APCI+, *m/z*): calculated for $C_{15}H_{13}$ $[M\text{-}HBr]^+$: 193.1012, found: 193.1005. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



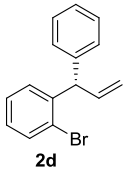
(+)-(*S*)-3-(4-bromophenyl)-3-phenylpropan-1-ol (4b): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4b** (33 mg, yield = 56%) as a colorless oil. 92:8 er, $[\alpha]_D^{20}$ = +3.6 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.35 (m, 2H), 7.34 – 7.17 (m, 5H), 7.16 – 7.09 (m, 2H), 4.12 (t, *J* = 7.9 Hz, 1H), 3.59 (t, *J* = 6.3 Hz, 2H), 2.28 (tt, *J* = 9.6, 4.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 143.6, 131.6, 129.6, 128.7, 128.6, 127.8, 126.5, 120.1, 60.8, 46.7, 38.0; HRMS (APCI–, *m/z*): calculated for $C_{15}H_{14}BrO$ $[M\text{-}H]^-$: 291.0202, found: 291.0203. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 210 nm, retention times (min): 80.02 (minor) and 84.81 (major).



(+)-(*S*)-1-bromo-3-(1-phenylallyl)benzene (2c): Purification by flash column chromatography (SiO_2, pentane) afforded only S_N2' product **2c** (42 mg, yield = 72%) as a colorless oil.[32] 91:9 er, $[\alpha]_D^{20}$ = +1.7 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 7.28 – 7.22 (m, 1H), 7.21 – 7.15 (m, 3H), 7.15 – 7.10 (m, 1H), 6.27 (ddd, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.27 (dt, *J* = 10.1, 1.3 Hz, 1H), 5.01 (dt, *J* = 17.1, 1.4 Hz, 1H), 4.71 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 142.4, 139.8, 131.6, 129.9, 129.5, 128.8, 128.6, 128.5, 127.3, 127.2, 126.6, 122.6, 117.0, 54.6; HRMS (APCI+, *m/z*): calculated for $C_{15}H_{13}$ $[M\text{-}HBr]^+$: 193.1012, found: 193.1008. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.

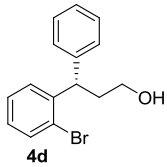


(+)-(*S*)-3-(3-bromophenyl)-3-phenylpropan-1-ol (4c): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4c** (25 mg, yield = 43%) as a colorless oil. 91:9 er, $[\alpha]_D^{20}$ = +2.2 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.0 Hz, 1H), 7.31 (dt, *J* = 10.1, 4.7 Hz, 3H), 7.26 – 7.10 (m, 5H), 4.12 (t, *J* = 7.8 Hz, 1H), 3.60 (t, *J* = 6.3 Hz, 2H), 2.30 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 143.6, 130.9, 130.1, 129.4, 128.7, 127.8, 126.6, 122.6, 60.7, 46.9, 38.0; HRMS (ESI–, *m/z*): calculated for $C_{15}H_{14}BrO$ $[M\text{-}H]^-$: 289.0223, found: 289.0228. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 210 nm, retention times (min): 56.61 (minor) and 59.57 (major).



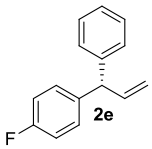
2d

(–)-(*S*)-1-bromo-2-(1-phenylallyl)benzene (2d): Purification by flash column chromatography (SiO_2, pentane) afforded a mixture of S_N2':S_N2 (99:1) **2d** (44 mg, yield = 72%) as a colorless oil.[32] 97:3 er, $[\alpha]_D^{20}$ = –13.5 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.29 – 7.23 (m, 2H), 7.23 – 7.18 (m, 3H), 7.11 (ddd, *J* = 8.0, 7.2, 1.9 Hz, 1H), 6.28 (ddd, *J* = 17.0, 10.2, 6.4 Hz, 1H), 5.30 (dt, *J* = 10.2, 1.5 Hz, 1H), 5.27 (dd, *J* = 6.3, 1.7 Hz, 1H), 4.94 (dt, *J* = 17.1, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 141.7, 139.4, 133.1, 130.4, 128.9, 128.9, 128.8, 128.4, 128.0, 127.4, 127.2, 126.5, 125.2, 117.2, 53.4; HRMS (APCI+, *m/z*): calculated for $C_{15}H_{13}$ [M-HBr]$^+$: 193.1012, found: 193.1011. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.

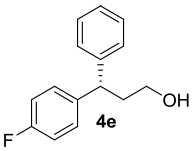


4d

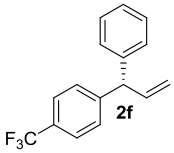
(–)-(*S*)-3-(2-bromophenyl)-3-phenylpropan-1-ol (4d): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4d** (37 mg, yield = 64%) as a colorless oil. 97:3 er, $[\alpha]_D^{20}$ = –48.9 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.39 – 7.24 (m, 7H), 7.20 (ddd, *J* = 8.6, 5.1, 3.3 Hz, 1H), 7.05 (ddd, *J* = 8.1, 7.0, 2.1 Hz, 1H), 4.68 (t, *J* = 7.8 Hz, 1H), 3.64 (t, *J* = 6.7 Hz, 2H), 2.30 (ddt, *J* = 17.8, 13.7, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 143.0, 133.1, 128.8, 128.5, 128.2, 127.8, 127.7, 126.5, 125.1, 60.9, 45.5, 38.3; HRMS (ESI+, *m/z*): calculated for $C_{15}H_{14}Br$ [M-H_2O]$^+$: 275.0253, found: 275.0252. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 210 nm, retention times (min): 65.27 (major) and 74.12 (minor).



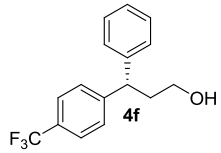
(–)-(*S*)-1-fluoro-4-(1-phenylallyl)benzene (2e): Purification by flash column chromatography (SiO_2, pentane) afforded a mixture of $S_N2':S_N2$ (98:2) **2e** (28 mg, yield = 60%) as a colorless oil.[32] 93:7 er, $[\alpha]_D^{20}$ = –1.0 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, J = 8.1, 6.7 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.20 – 7.10 (m, 4H), 7.04 – 6.93 (m, 2H), 6.28 (ddd, J = 17.2, 10.2, 7.1 Hz, 1H), 5.24 (dt, J = 10.2, 1.4 Hz, 1H), 4.99 (dt, J = 17.1, 1.5 Hz, 1H), 4.73 (d, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 160.3, 143.1, 141.2, 140.5, 139.0, 138.9, 130.1, 130.0, 128.7, 128.5, 127.2, 126.5, 116.5, 115.2, 115.0, 54.2; ^{19}F NMR (400 MHz, $CDCl_3$) δ -116.95 (tt, J = 8.7, 5.3 Hz, 1F); HRMS (APCI–, *m/z*): calculated for $C_{15}H_{12}F$ $[M\text{-}H]^-$: 211.0918, found: 211.0922. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



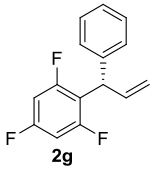
(+)-(*S*)-3-(4-fluorophenyl)-3-phenylpropan-1-ol (4e): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4e** (22 mg, yield = 47%) as a colorless oil. 93:7 er, $[\alpha]_D^{20}$ = +1.2 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.25 – 7.14 (m, 4H), 7.02 – 6.91 (m, 2H), 4.13 (t, J = 8.0 Hz, 1H), 3.61 (t, J = 6.4 Hz, 1H), 2.29 (dtd, J = 9.0, 6.4, 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 160.1, 144.2, 140.2, 140.1, 129.2, 128.6, 127.7, 126.4, 115.3, 115.2, 61.0, 46.5, 38.2, 20.5; ^{19}F NMR (400 MHz, $CDCl_3$) δ -117.01 (ddd, J = 13.9, 8.8, 5.4 Hz, 1F); HRMS (ESI–, *m/z*): calculated for $C_{15}H_{14}FO$ $[M\text{-}H]^-$: 229.1023, found: 229.1031. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 210 nm, retention times (min): 36.60 (minor) and 43.20 (major).



(–)-(*S*)-1-(1-phenylallyl)-4-(trifluoromethyl)benzene (2f): Purification by flash column chromatography (SiO_2, pentane) afforded a mixture of $S_N2':S_N2$ (99:1) **2f** (37 mg, yield = 71%) as a colorless oil.[32] 95:5 er, $[\alpha]_D^{20}$ = –7.1 (c = 1 in $CHCl_3$); [lit.[10d] (93% ee): $[\alpha]_D^{21}$ = –8.0 (c = 1.42 in $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 2H), 7.39 – 7.29 (m, 4H), 7.25 (tt, J = 6.4, 1.4 Hz, 1H), 7.22 – 7.15 (m, 2H), 6.30 (ddd, J = 17.2, 10.2, 7.2 Hz, 1H), 5.29 (dt, J = 10.2, 1.3 Hz, 1H), 5.03 (dt, J = 17.1, 1.4 Hz, 1H), 4.81 (d, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 147.4, 142.3, 139.7, 128.9, 128.7, 128.6, 128.5, 127.2, 126.7, 125.4, 125.4, 125.3, 125.3, 117.1, 54.7; ^{19}F NMR (400 MHz, $CDCl_3$) δ -62.4. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.

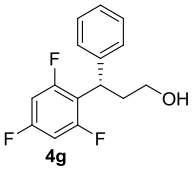


(–)-(*S*)-3-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-ol (4f): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4f** (35 mg, yield = 66%) as a colorless oil. 95:5 er, $[\alpha]_D^{20}$ = –1.2 (c = 1 in $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.27 – 7.17 (m, 3H), 4.23 (t, J = 7.9 Hz, 1H), 3.61 (t, J = 6.4 Hz, 1H), 2.33 (dtd, J = 7.7, 6.4, 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 148.6, 143.4, 128.7, 128.2, 127.8, 126.7, 125.5, 125.5, 125.4, 125.4, 60.6, 47.1, 37.9; ^{19}F NMR (400 MHz, $CDCl_3$) δ -62.4; HRMS (ESI–, *m/z*): calculated for $C_{16}H_{14}F_3O$ $[M\text{-}H]^-$: 279.0991, found: 279.0998. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 210 nm, retention times (min): 35.12 (minor) and 46.39 (major).



2g

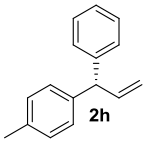
(–)-(*S*)-1,3,5-trifluoro-2-(1-phenylallyl)benzene (2g): Purification by flash column chromatography (SiO_2, pentane) afforded a mixture of $S_N2':S_N2$ (96:4) **2g** (41 mg, yield = 81%) as a colorless oil.[32] 98:2 er, $[\alpha]_D^{20}$ = –29.5 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.29 – 7.20 (m, 3H), 6.67 (t, *J* = 8.5 Hz, 2H), 6.43 (dddt, *J* = 17.0, 10.0, 7.8, 2.1 Hz, 1H), 5.28 (dt, *J* = 10.1, 1.2 Hz, 1H), 5.20 (dt, *J* = 17.1, 1.1 Hz, 1H), 5.11 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 162.7, 162.5, 162.5, 162.3, 162.3, 162.2, 160.4, 160.2, 160.1, 160.0, 159.9, 159.8, 159.7, 141.2, 137.1, 128.7, 128.4, 127.5, 127.2, 126.6, 117.3, 100.8, 100.6, 100.5, 100.3, 100.2, 44.0, 43.9; ^{19}F NMR (400 MHz, $CDCl_3$) δ -109.37 (t, *J* = 6.8 Hz, 2F), -110.26 – -110.47 (m, 1F); HRMS (APCI+, *m/z*): calculated for $C_{15}H_{10}F$ $[M\text{-}2HF]^+$: 209.0761, found: 209.0762. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



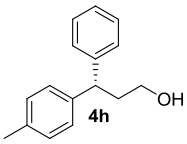
4g

(–)-(*S*)-3-phenyl-3-(2,4,6-trifluorophenyl)propan-1-ol (4g): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4g** (31 mg, yield = 61%) as a colorless oil. 98:2 er, $[\alpha]_D^{20}$ = –27.0 (c = 1 in $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.4 Hz, 3H), 7.41 – 7.33 (m, 2H), 7.33 – 7.25 (m, 1H), 6.76 – 6.65 (m, 2H), 4.66 (t, *J* = 8.1 Hz, 1H), 3.82 – 3.60 (m, 2H), 2.64 – 2.38 (m, 2H), 1.78 – 1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 162.6, 162.5, 162.4, 162.3, 160.2, 160.0, 159.9, 142.1, 128.5, 127.7, 126.6, 116.1, 116.0, 100.8, 100.5, 100.3, 100.2, 60.9, 36.42, 35.3; ^{19}F NMR (400 MHz, $CDCl_3$) δ -109.28 – -109.59 (m, 2f), -110.46 – -110.74 (m, 1F); HRMS (ESI–, *m/z*): calculated for $C_{15}H_{11}F_2O$ $[M\text{-}HF]^-$: 245.0773,

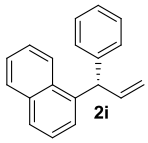
found: 245.0780. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 210 nm, retention times (min): 32.52 (minor) and 34.80 (major).



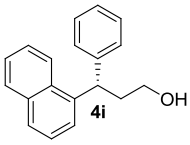
(–)-(*S*)-1-methyl-4-(1-phenylallyl)benzene (2h): Purification by flash column chromatography (SiO_2, pentane) afforded only S_N2' product **2h** (37 mg, yield = 83%) as a colorless oil. 92:8 er, $[\alpha]_D^{20}$ = –1.8 (c = 1 in $CHCl_3$); [lit.[10b] (91% ee): $[\alpha]_D^{20}$ = –2.2 (c = 1.09 in $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.27 – 7.19 (m, 3H), 7.17 – 7.08 (m, 4H), 6.32 (ddd, *J* = 17.2, 10.2, 7.3 Hz, 1H), 5.24 (dt, *J* = 10.2, 1.4 Hz, 1H), 5.02 (dt, *J* = 17.1, 1.5 Hz, 1H), 4.73 (d, *J* = 7.2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 140.8, 140.3, 135.9, 129.1, 128.6, 128.5, 128.4, 126.3, 116.2, 54.6, 21.0; HRMS (APCI+, *m/z*): calculated for $C_{16}H_{17}$ $[M+H]^+$: 209.1325, found: 209.1327. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



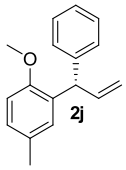
(+)-(*S*)-3-phenyl-3-p-tolylpropan-1-ol (4h): Purification by flash column chromatography (SiO_2, 30% EtOAc/pentane) afforded **4h** (23 mg, yield = 50%) as a colorless oil. 92:8 er, $[\alpha]_D^{20}$ = +1.6 (c = 1 in $CHCl_3$); [lit.[10b] (91% ee): $[\alpha]_D^{20}$ = +4.3 (c = 1.24 in $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 4H), 7.20 – 7.12 (m, 3H), 7.09 (d, *J* = 7.9 Hz, 2H), 4.10 (t, *J* = 8.0 Hz, 1H), 3.62 (t, *J* = 6.4 Hz, 2H), 2.31 (d, *J* = 6.8 Hz, 5H), 1.45 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 141.4, 135.8, 129.2, 128.5, 127.8, 127.7, 126.2, 61.2, 47.0, 38.3, 21.0; HRMS (ESI–, *m/z*): calculated for $C_{16}H_{17}O$ $[M-H]^-$: 225.1274, found: 225.1282. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 222 nm, retention times (min): 66.63 (minor) and 70.20 (major).



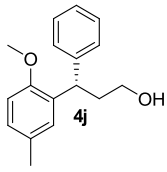
(+)-(*S*)-1-(1-phenylallyl)naphthalene (2i): Purification by flash column chromatography (SiO_2, pentane) afforded a mixture of S_N2':S_N2 (99:1) **2i** (37 mg, yield = 64%) as a colorless oil. 96:4 er, $[\alpha]_D^{20}$ = +27.9 (c = 1 in $CHCl_3$); [lit.[10d] (93% ee): $[\alpha]_D^{25}$ = +32.0 (c = 0.66 in $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.99 (m, 1H), 7.92 – 7.84 (m, 1H), 7.78 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.51 – 7.40 (m, 3H), 7.36 (dt, *J* = 7.3, 0.9 Hz, 1H), 7.33 – 7.18 (m, 5H), 6.45 (ddd, *J* = 17.0, 10.2, 6.4 Hz, 1H), 5.52 (d, *J* = 6.4 Hz, 1H), 5.29 (dt, *J* = 10.2, 1.4 Hz, 1H), 4.92 (dt, *J* = 17.1, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 140.6, 138.9, 134.0, 131.7, 128.8, 128.7, 128.7, 128.4, 128.4, 127.3, 126.4, 126.3, 125.9, 125.4, 125.3, 124.1, 116.9, 50.8. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



(–)-(*S*)-3-(naphthalen-1-yl)-3-phenylpropan-1-ol (4i): Purification by flash column chromatography (SiO_2, 30% EtOAc/pentane) afforded **4i** (30 mg, yield = 58%) as a colorless oil. 96:4 er, $[\alpha]_D^{20}$ = –25.8 (c = 1 in $CHCl_3$); [lit.[10d] (93% ee): $[\alpha]_D^{25}$ = –37.4 (c = 0.57 in $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.20 (m, 1H), 7.92 (dt, *J* = 7.9, 3.2 Hz, 1H), 7.88 – 7.77 (m, 1H), 7.68 – 7.48 (m, 4H), 7.45 – 7.30 (m, 4H), 7.24 (t, *J* = 7.2 Hz, 1H), 5.07 (t, *J* = 7.6 Hz, 1H), 3.77 (t, *J* = 6.4 Hz, 2H), 2.65 – 2.37 (m, 2H), 1.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 140.1, 134.2, 132.0, 128.9, 128.6, 128.2, 127.2, 126.3, 126.1, 125.5, 125.4, 124.5, 123.8, 61.1, 42.3, 38.9. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OJ-H column, *n*-heptane/*i*-PrOH 95:5, 40 °C, 220 nm, retention times (min): 51.94 (minor) and 65.57 (major).

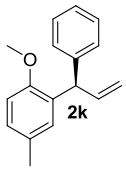


(+)-(*S*)-1-methoxy-4-methyl-2-(1-phenylallyl)benzene (2j): Purification by flash column chromatography (SiO_2, 20% toluene/pentane) afforded a mixture of S_N2': S_N2 (99:1) **2j** (41 mg, yield = 73%) as a colorless oil. 96:4 er, $[\alpha]_D^{20}$ = +24.8 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.20 (dt, *J* = 7.9, 1.9 Hz, 3H), 7.04 – 6.98 (m, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.31 (ddd, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.20 (dt, *J* = 10.2, 1.5 Hz, 1H), 5.14 (d, *J* = 6.9 Hz, 1H), 4.94 (dt, *J* = 17.1, 1.7 Hz, 1H), 3.73 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.89, 143.2, 140.5, 131.5, 129.9, 129.6, 128.6, 128.1, 127.8, 125.9, 115.9, 110.9, 55.8, 47.6, 20.7; HRMS (APPI–, *m/z*): calculated for $C_{17}H_{17}O$ $[M-H]^-$: 237.1274, found: 237.1278. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.

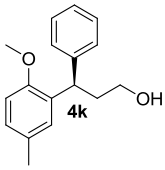


(–)-(*S*)-3-(2-methoxy-5-methylphenyl)-3-phenylpropan-1-ol (4j): Purification by flash column chromatography (SiO_2, 30% EtOAc/pentane) afforded **4j** (28 mg, yield = 55%) as a colorless oil. 96:4 er, $[\alpha]_D^{20}$ = –23.4 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 4H), 7.22 – 7.13 (m, 1H), 7.00 – 6.90 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 1H), 4.60 (dd, *J* = 8.9, 7.1 Hz, 1H), 3.80 (s, 3H), 3.62 (dt, *J* = 11.6, 5.9 Hz, 1H), 3.53 (ddd, *J* = 11.0, 7.6, 5.8 Hz, 1H), 2.33 (dtd, *J* = 13.6, 7.3, 6.3 Hz, 1H), 2.24 (s, 3H), 2.23 – 2.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 144.6, 132.6, 130.1, 128.8, 128.2, 128.1, 127.6, 125.9, 110.8, 61.2, 55.8, 38.9, 37.8, 20.7; HRMS (APCI+, *m/z*): calculated for $C_{17}H_{19}O$ $[M+H]^+$: 239.1430, found: 239.1432. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-

heptane/*i*-PrOH 99:1, 40 °C, 220 nm, retention times (min): 55.75 (minor) and 59.55 (major).

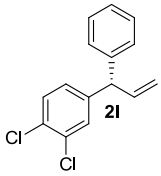


(–)-(*R*)-1-methoxy-4-methyl-2-(1-phenylallyl)benzene (2k): Reaction performed on 5 mmol scale (1.2 g of **1j**). Purification by flash column chromatography (SiO_2, 20% toluene/pentane) afforded a mixture of S_N2':S_N2 (99:1) **2k** (910 mg, yield = 80%) as a colorless oil. 96:4 er, $[\alpha]_D^{20}$ = –18.1 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.20 (dt, *J* = 7.9, 1.9 Hz, 3H), 7.04 – 6.98 (m, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.31 (ddd, *J* = 17.0, 10.1, 6.8 Hz, 1H), 5.20 (dt, *J* = 10.2, 1.5 Hz, 1H), 5.14 (d, *J* = 6.9 Hz, 1H), 4.94 (dt, *J* = 17.1, 1.7 Hz, 1H), 3.73 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.89, 143.2, 140.5, 131.5, 129.9, 129.6, 128.6, 128.1, 127.8, 125.9, 115.9, 110.9, 55.8, 47.6, 20.7; HRMS (APPI–, *m/z*): calculated for $C_{17}H_{17}O$ $[M\text{-}H]^-$: 237.1274, found: 237.1280. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.

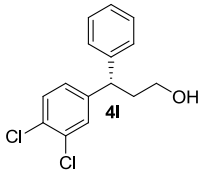


(+)-(*R*)-3-(2-methoxy-5-methylphenyl)-3-phenylpropan-1-ol (4k): Purification by flash column chromatography (SiO_2, 30% EtOAc/pentane) afforded **4k** (28 mg, yield = 78%) as a colorless oil. 96:4 er, $[\alpha]_D^{20}$ = +23.8 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 4H), 7.22 – 7.13 (m, 1H), 7.00 – 6.90 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 1H), 4.60 (dd, *J* = 8.9, 7.1 Hz, 1H), 3.80 (s, 3H), 3.62 (dt, *J* = 11.6, 5.9 Hz, 1H), 3.53 (ddd, *J* = 11.0, 7.6, 5.8 Hz, 1H), 2.33 (dtd, *J* = 13.6, 7.3, 6.3 Hz, 1H), 2.24 (s, 3H), 2.23 – 2.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 144.6, 132.6, 130.1, 128.8, 128.2, 128.1, 127.6, 125.9, 110.8, 61.2, 55.8, 38.9, 37.8, 20.7; HRMS (APCI+, *m/z*): calculated for

$C_{17}H_{19}O$ $[M+H]^+$: 239.1430, found: 239.1433. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 220 nm, retention times (min): 57.74 (major) and 61.87 (minor).

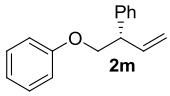


(–)-(*S*)-1,2-dichloro-4-(1-phenylallyl)benzene (2l): Purification by flash column chromatography (SiO_2, pentane) afforded only S_N2' product **2l** (39 mg, yield = 69%) as a colorless oil.[32] 93:7 er, $[\alpha]_D^{20}$ = –2.0 (c = 1 in $CHCl_3$); [lit.[10d] (92% ee): $[\alpha]_D^{20}$ = –3.9 (c = 1.44 in $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 3H), 7.29 (d, *J* = 2.1 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.20 – 7.12 (m, 2H), 7.02 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.24 (ddd, *J* = 17.1, 10.2, 7.1 Hz, 1H), 5.28 (dt, *J* = 10.2, 1.3 Hz, 1H), 5.01 (dt, *J* = 17.1, 1.4 Hz, 1H), 4.69 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.0, 139.5, 132.4, 130.5, 130.4, 130.3, 128.7, 128.6, 128.5, 128.5, 128.1, 127.2, 127.2, 126.8, 117.3, 54.0. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.

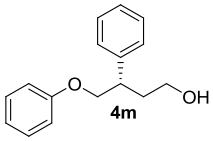


(+)-(*S*)-3-(3,4-dichlorophenyl)-3-phenylpropan-1-ol (4l): Purification by flash column chromatography (SiO_2, 30% EtOAc/pentane) afforded **4l** (31 mg, yield = 54%) as a colorless oil. 93:7 er, $[\alpha]_D^{20}$ = +5.0 (c = 1 in $CHCl_3$); [lit.[10d] (92% ee): $[\alpha]_D^{25}$ = +6.5 (c = 1.48 in CH_2Cl_2)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.09 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.13 (t, *J* = 7.9 Hz, 1H), 3.59 (t, *J* = 6.3 Hz, 2H), 2.27 (dtd, *J* = 8.0, 6.3, 4.1 Hz, 2H), 1.54 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.2, 132.4, 130.4, 130.2, 129.8, 128.8, 127.8, 127.3, 126.8, 60.5, 46.3, 37.8. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OJ-H column, *n*-

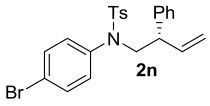
heptane/*i*-PrOH 98:2, 40 °C, 220 nm, retention times (min): 47.81 (major) and 53.40 (minor).



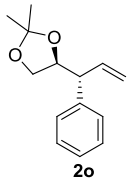
(+)-(*S*)-(1-phenoxybut-3-en-2-yl)benzene (2m): Purification by flash column chromatography (SiO_2, 10% toluene/pentane) afforded only S_N2' product **2m** (41 mg, yield = 90%) as a colorless oil. 80:20 er, $[\alpha]_D^{20}$ = +10.0 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.18 (m, 7H), 7.03 – 6.82 (m, 3H), 6.15 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1H), 5.28 – 5.12 (m, 2H), 4.31 – 4.13 (m, 2H), 3.85 (q, *J* = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 140.8, 138.3, 129.4, 128.6, 128.1, 126.9, 120.8, 116.5, 114.7, 71.0, 49.1; HRMS (APCI–, *m/z*): calculated for $C_{16}H_{15}O$ $[M-H]^-$: 223.1117, found: 223.1121. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



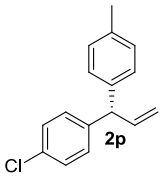
(+)-(*S*)-4-phenoxy-3-phenylbutan-1-ol (4m): Purification by flash column chromatography (SiO_2, 30% EtOAc/pentane) afforded **4m** (24 mg, yield = 50%) as a colorless oil. 80:20 er, $[\alpha]_D^{20}$ = +13.5 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.9, 6.7 Hz, 2H), 7.32 – 7.22 (m, 5H), 6.95 (td, *J* = 7.3, 1.1 Hz, 1H), 6.92 – 6.87 (m, 2H), 4.23 – 3.99 (m, 2H), 3.68 (dt, *J* = 10.6, 6.1 Hz, 1H), 3.60 (ddd, *J* = 10.7, 7.5, 6.1 Hz, 1H), 3.27 (ddt, *J* = 9.0, 7.2, 5.5 Hz, 1H), 2.33 – 2.15 (m, 1H), 1.99 (ddt, *J* = 13.7, 9.2, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 141.8, 129.5, 128.7, 127.9, 126.9, 120.9, 114.6, 72.3, 60.9, 42.4, 35.8; HRMS (APCI+, *m/z*): calculated for $C_{16}H_{17}O$ $[M-H_2O]^+$: 225.1274, found: 225.1270. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 210 nm, retention times (min): 72.42 (minor) and 74.72 (major).



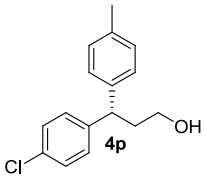
(–)-(*S*)-*N*-(4-bromophenyl)-4-methyl-*N*-(2-phenylbut-3-enyl)benzenesulfonamide (2n): Purification by flash column chromatography (SiO_2, 10% EtOAc/pentane) afforded only S_N2' product **2n** (81 mg, yield = 88%) as a colorless oil. 86:14 er, $[\alpha]_D^{20}$ = –1.7 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 4H), 7.32 – 7.25 (m, 2H), 7.25 – 7.18 (m, 3H), 7.16 – 7.06 (m, 2H), 6.87 – 6.75 (m, 2H), 5.98 (ddd, *J* = 17.1, 10.3, 7.7 Hz, 1H), 5.14 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.04 (dt, *J* = 17.1, 1.3 Hz, 1H), 3.91 (dd, *J* = 13.2, 8.8 Hz, 1H), 3.68 (dd, *J* = 13.2, 7.1 Hz, 1H), 3.35 (q, *J* = 7.8 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 140.6, 138.3, 138.2, 134.7, 132.1, 130.6, 129.5, 128.7, 127.9, 127.7, 127.0, 121.8, 116.9, 54.7, 48.5, 21.6; HRMS (APCI+, *m/z*): calculated for $C_{23}H_{22}BrNO_2SNa$ $[M+Na+H]^+$: 480.0426, found: 480.0423. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 254 nm, retention times (min): 58.34 (minor) and 60.77 (major).



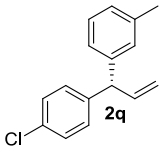
(–)-(*S*)-2,2-dimethyl-4-((*R*)-1-phenylallyl)-1,3-dioxolane (2o): Purification by flash column chromatography (SiO_2, 2% Et_2O/pentane) afforded a mixture of *anti*:*syn* = >98:~2 **2o** (37 mg, yield = 90%) as a colorless oil. $[\alpha]_D^{20}$ = –52.5 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (tt, *J* = 7.0, 1.0 Hz, 2H), 7.26 – 7.18 (m, 3H), 6.16 (ddd, *J* = 17.5, 10.3, 7.4 Hz, 1H), 5.18 (ddd, *J* = 10.3, 1.6, 1.1 Hz, 1H), 5.10 (dt, *J* = 17.2, 1.4 Hz, 1H), 4.40 (ddd, *J*= 8.3, 6.8, 6.0 Hz, 1H), 3.79 (dd, *J* = 8.4, 6.1 Hz, 1H), 3.58 (dd, *J* = 8.4, 6.9 Hz, 1H), 3.42 – 3.30 (t, *J* = 7.8 Hz, 1H), 1.45 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 138.4, 128.7, 128.2, 127.0, 116.5, 109.6, 78.5, 68.1, 53.8, 26.8, 25.7; HRMS (APPI–, *m/z*): calculated for $C_{14}H_{17}O_2$ $[M-H]^-$: 217.1223, found: 217.1228.



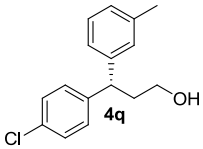
(–)-(*S*)-1-chloro-4-(1-*p*-tolylallyl)benzene (2p): Purification by flash column chromatography (SiO_2, pentane) afforded only S_N2' product **2p** (32 mg, yield = 64%) as a colorless oil. 97:3 er, $[\alpha]_D^{20}$ = –4.3 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 3H), 7.18 – 7.09 (m, 3H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.25 (ddd, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.22 (dt, *J* = 10.2, 1.4 Hz, 1H), 4.98 (dt, *J* = 17.1, 1.5 Hz, 1H), 4.67 (d, *J* = 7.1 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 140.3, 139.8, 136.1, 132.0, 129.90, 129.2, 128.5, 128.4, 116.5, 53.9, 21.0; HRMS (APCI+, *m/z*): calculated for $C_{16}H_{14}$ $[M\text{-}HCl]^-$: 206.1090, found: 206.1092. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



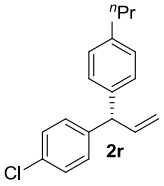
(+)-(*S*)-3-(4-chlorophenyl)-3-*p*-tolylpropan-1-ol (4p): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4p** (20 mg, yield = 45%) as a colorless oil. 97:3 er, $[\alpha]_D^{20}$ = +0.5 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 2H), 7.19 – 7.14 (m, 2H), 7.10 (s, 4H), 4.08 (t, *J* = 7.9 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.30 (s, 3H), 2.28 – 2.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 140.9, 136.0, 131.9, 129.3, 129.1, 128.6, 127.6, 60.9, 46.2, 38.1, 20.9; HRMS (APCI–, *m/z*): calculated for $C_{16}H_{16}ClO$ $[M\text{-}H]^-$: 259.0884, found: 259.0887. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 203 nm, retention times (min): 34.40 (minor) and 39.86 (major).



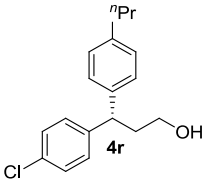
(–)-(*R*)-1-(1-(4-chlorophenyl)allyl)-3-methylbenzene (2q): Purification by flash column chromatography (SiO_2, pentane) afforded only S_N2' product **2q** (43 mg, yield = 75%) as a colorless oil. 97:3 er, $[\alpha]_D^{20}$ = –11.6 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.16 – 7.09 (m, 2H), 7.05 (dp, *J* = 7.5, 0.9 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.26 (ddd, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.24 (dt, *J* = 10.2, 1.4 Hz, 1H), 4.99 (dt, *J* = 17.1, 1.5 Hz, 1H), 4.67 (d, *J* = 7.2 Hz, 1H), 2.36 – 2.29 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 141.9, 140.2, 138.1, 132.1, 129.9, 129.2, 128.5, 128.4, 127.3, 125.5, 116.6, 54.3, 21.5; HRMS (APCI+, *m/z*): calculated for $C_{16}H_{14}$ [M-HCl]$^+$: 206.1090, found: 206.1092. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



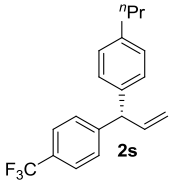
(+)-(*R*)-3-(4-chlorophenyl)-3-*m*-tolylpropan-1-ol (4q): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4q** (36 mg, yield = 81%) as a colorless oil. 97:3 er, $[\alpha]_D^{20}$ = +3.7 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 2H), 7.22 – 7.14 (m, 3H), 7.06 – 6.97 (m, 3H), 4.08 (t, *J* = 7.9 Hz, 1H), 3.59 (t, *J* = 6.4 Hz, 2H), 2.32 (s, 3H), 2.30 – 2.21 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 143.2, 138.2, 131.9, 129.2, 128.6, 128.6, 128.5, 127.3, 124.7, 60.9, 46.6, 38.1, 21.5; HRMS (APCI–, *m/z*): calculated for $C_{16}H_{16}ClO$ [M-H]$^-$: 259.0884, found: 259.0886. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 220 nm, retention times (min): 28.46 (minor) and 32.11 (major).



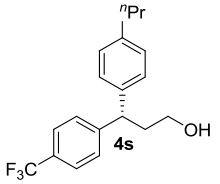
(–)-(*S*)-1-chloro-4-(1-(4-*n*-propylphenyl)allyl)benzene (2r): Purification by flash column chromatography (SiO_2, pentane) afforded only S_N2' product **2r** (41 mg, yield = 76%) as a colorless oil.[33] 95:5 er, $[\alpha]_D^{20}$ = –5.0 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 3H), 7.23 – 7.06 (m, 8H), 6.28 (ddd, *J* = 17.2, 10.1, 7.2 Hz, 1H), 5.25 (dt, *J* = 10.1, 1.3 Hz, 1H), 5.01 (dt, *J* = 17.1, 1.5 Hz, 1H), 4.70 (d, *J* = 7.2 Hz, 1H), 2.62 – 2.54 (m, 3H), 1.79 – 1.58 (m, 4H), 1.05 – 0.93 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 142.0, 141.0, 140.4, 132.1, 130.0, 128.6, 128.5, 128.3, 116.5, 54.0, 37.7, 24.6, 14.0; HRMS (APCI+, *m/z*): calculated for $C_{18}H_{19}$ $[M\text{-}HCl]^+$: 235.1481, found: 235.1476. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



(+)-(*S*)-3-(4-chlorophenyl)-3-(4-propylphenyl)propan-1-ol (4r): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4r** (32 mg, yield = 70%) as a colorless oil. 95:5 er, $[\alpha]_D^{20}$ = +0.5 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 7.20 – 7.15 (m, 2H), 7.15 – 7.06 (m, 4H), 4.09 (t, *J* = 7.9 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.54 (dd, *J* = 8.5, 6.8 Hz, 2H), 2.27 (dtd, *J* = 7.8, 6.4, 4.6 Hz, 2H), 1.67 – 1.52 (m, 3H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 141.1, 140.9, 131.9, 129.2, 128.7, 128.6, 127.5, 61.0, 46.3, 38.1, 37.6, 24.5, 13.9; HRMS (APCI–, *m/z*): calculated for $C_{18}H_{20}ClO$ $[M\text{-}H]^-$: 287.1197, found: 287.1198. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OJ-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 205 nm, retention times (min): 27.04 (major) and 30.43 (minor).

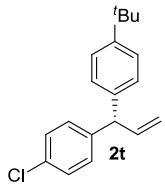


(–)-(*S*)-1-propyl-4-(1-(4-(trifluoromethyl)phenyl)allyl)benzene (2s): Purification by flash column chromatography (SiO_2, pentane) afforded a mixture of $S_N2':S_N2$ (90:10) **2s** (52 mg, yield = 58%) as a colorless oil.[33] 96:4 er, $[\alpha]_D^{20}$ = –4.6 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.51 (m, 3H), 7.37 – 7.29 (m, 2H), 7.30 – 7.26 (m, 1H), 7.23 – 7.13 (m, 4H), 7.11 (dd, *J* = 8.1, 1.3 Hz, 4H), 6.31 (ddd, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.28 (dt, *J* = 10.1, 1.3 Hz, 1H), 5.03 (dt, *J* = 17.0, 1.4 Hz, 1H), 4.78 (d, *J* = 7.2 Hz, 1H), 4.00 – 3.67 (m, 0.5H), 3.57 (dd, *J* = 3.7, 1.6 Hz, 0.2H), 2.65 – 2.43 (m, 4H), 1.76 – 1.53 (m, 4H), 1.10 – 0.89 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 147.6, 142.9, 141.5, 141.2, 140.2, 140.0, 139.6, 138.6, 128.9, 128.8, 128.8, 128.7, 128.7, 128.5, 128.4, 128.4, 128.3, 127.6, 126.8, 126.2, 125.4, 125.3, 125.3, 125.3, 116.9, 54.4, 50.7, 37.7, 37.7, 35.7, 30.3, 24.6, 22.8, 14.0, 14.0, 13.9, 13.9; ^{19}F NMR (400 MHz, $CDCl_3$) δ -62.3, -62.4; HRMS (ESI–, *m/z*): calculated for $C_{19}H_{18}F_3$ $[M\text{-}H]^-$: 303.1355, found: 303.1361. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.

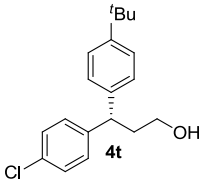


(–)-(*S*)-3-(4-propylphenyl)-3-(4-(trifluoromethyl)phenyl)propan-1-ol (4s): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4s** (21 mg, yield = 50%) as a colorless oil. 96:4 er, $[\alpha]_D^{20}$ = –3.1 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.20 – 7.05 (m, 4H), 4.19 (t, *J* = 7.9 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.73 – 2.45 (m, 2H), 2.31 (dtd, *J* = 7.7, 6.3, 5.3 Hz, 2H), 1.76 – 1.52 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 141.1, 140.5, 128.8, 128.6, 128.3,

128.1, 127.6, 125.5, 125.4, 125.4, 125.4, 60.7, 46.7, 38.0, 37.6, 24.5, 13.9; ^{19}F NMR (400 MHz, $CDCl_3$) δ -62.40; HRMS (APCI–, *m/z*): calculated for $C_{19}H_{20}F_3O$ $[M\text{-}H]^-$: 321.1461, found: 321.1461. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OJ column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 220 nm, retention times (min): 21.29 (major) and 23.94 (minor).

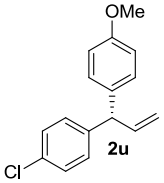


(–)-(*S*)-1-tert-butyl-4-(1-(4-chlorophenyl)allyl)benzene (2t): Purification by flash column chromatography (SiO_2, pentane) afforded only S_N2' product **2t** (32 mg, yield = 56%) as a colorless oil. 99:1 er, $[\alpha]_D^{20}$ = –6.7 (c = 1 in $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.24 (m, 2H), 7.18 – 7.07 (m, 4H), 6.27 (ddd, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.23 (dt, *J* = 10.2, 1.3 Hz, 1H), 5.00 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.68 (d, *J* = 7.2 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 142.0, 140.3, 139.7, 132.1, 130.0, 128.5, 128.0, 125.4, 116.5, 53.9, 34.4, 31.4; HRMS (APCI+, *m/z*): calculated for $C_{19}H_{22}Cl$ $[M\text{-}H]^-$: 285.1405, found: 285.1412. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.

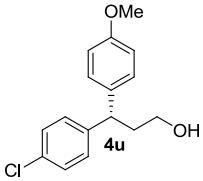


(–)-(*S*)-3-(4-*tert*-butylphenyl)-3-(4-chlorophenyl)propan-1-ol (4t): Purification by flash column chromatography (SiO_2, 20% EtOAc/pentane) afforded **4t** (26 mg, yield = 54%) as a colorless oil. 99:1 er, $[\alpha]_D^{20}$ = –5.5 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 7.21 – 7.17 (m, 2H), 7.17 – 7.13 (m, 2H), 4.09 (t, *J* = 7.9 Hz, 1H), 3.59 (td, *J*= 6.5, 1.5 Hz, 2H), 2.27 (dq, *J* = 8.1, 6.5 Hz, 2H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3,

143.2, 140.8, 131.9, 129.2, 128.6, 127.3, 125.5, 60.9, 46.2, 38.2, 34.4, 31.3; HRMS (APCI–, *m/z*): calculated for $C_{19}H_{22}ClO$ $[M\text{-}H]^-$: 301.1354, found: 301.1353. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OJ column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 225 nm, retention times (min): 25.04 (minor) and 27.68 (major).

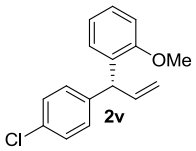


(–)-(*S*)-1-chloro-4-(1-(4-methoxyphenyl)allyl)benzene (2u): Purification by flash column chromatography (SiO_2, 10% toluene/pentane) afforded only S_N2' product **2u** (31 mg, yield = 60%) as a colorless oil. 96:4 er, $[\alpha]_D^{20}$ = –4.2 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 2H), 7.17 – 6.99 (m, 4H), 6.92 – 6.76 (m, 2H), 6.24 (ddd, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.22 (dt, *J* = 10.2, 1.3 Hz, 1H), 4.97 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.66 (d, *J* = 7.1 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 142.1, 140.4, 134.8, 132.1, 129.9, 129.4, 128.5, 116.4, 113.9, 55.2, 53.4; HRMS (APCI+, *m/z*): calculated for $C_{16}H_{16}ClO$ $[M\text{-}H]^+$: 259.0884, found: 259.0886. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.

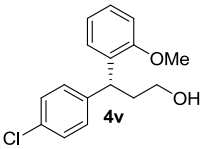


(+)-(*S*)-3-(4-chlorophenyl)-3-(4-methoxyphenyl)propan-1-ol (4u): Purification by flash column chromatography (SiO_2, 30% EtOAc/pentane) afforded **4u** (29 mg, yield = 87%) as a colorless oil. 96:4 er, $[\alpha]_D^{20}$ = +5.0 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 7.21 – 7.09 (m, 4H), 6.89 – 6.78 (m, 2H), 4.07 (t, *J* = 7.9 Hz, 1H), 3.77 (s, 3H), 3.59 (t, *J* = 6.5 Hz, 2H), 2.25 (dtd, *J* = 8.0, 6.4, 1.7 Hz, 2H), 1.31 – 1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 143.4, 136.0, 130.6, 129.1, 128.7, 128.6, 114.0, 60.9, 55.2, 45.7, 38.1;

HRMS (APCI–, *m/z*): calculated for $C_{16}H_{16}ClO_2$ $[M-H]^-$: 275.0833, found: 275.0835. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OJ-H column, *n*-heptane/*i*-PrOH 90:10, 40 °C, 230 nm, retention times (min): 20.22 (major) and 22.80 (minor).

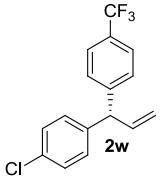


(+)-(*R*)-1-(1-(4-chlorophenyl)allyl)-2-methoxybenzene (2v): Purification by flash column chromatography (SiO_2, 2% Et_2O/pentane) afforded a mixture of S_N2':S_N2 (80:20) **2v** (47 mg, yield = 92%) as a colorless oil. 63:37 er, $[\alpha]_D^{20}$ = +5.0 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 4H), 7.15 (td, *J* = 8.4, 7.8, 1.9 Hz, 3H), 6.96 (td, *J*= 7.4, 1.1 Hz, 1H), 6.89 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.29 (ddd, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.24 (dt, *J* = 10.1, 1.5 Hz, 1H), 5.14 (d, *J* = 6.7 Hz, 1H), 4.94 (dt, *J* = 17.1, 1.6 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 156.9, 141.6, 140.0, 131.7, 131.2, 130.0, 129.9, 129.7, 129.4, 129.1, 128.6, 128.2, 127.8, 127.6, 127.3, 120.6, 120.5, 116.4, 110.8, 110.4, 55.5, 55.4, 47.1, 33.5; HRMS (APCI+, *m/z*): calculated for $C_{16}H_{16}ClO$ $[M+H]^+$: 259.0884, found: 259.0883. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.

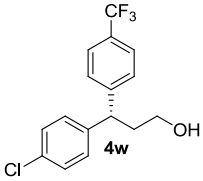


(–)-(*R*)-3-(4-chlorophenyl)-3-(2-methoxyphenyl)propan-1-ol (4v): Purification by flash column chromatography (SiO_2, 30% EtOAc/pentane) afforded **4v** (25 mg, yield = 57%) as a colorless oil. 63:37 er, $[\alpha]_D^{20}$ = –16.6 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 5H), 7.18 – 7.11 (m, 1H), 6.92 (td, *J* = 7.5, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.3, 1.1 Hz, 1H), 4.58 (t, *J* = 7.9 Hz, 1H), 3.80 (s, 3H), 3.67 – 3.48 (m, 2H), 2.38 – 2.14 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 143.0, 132.2, 131.6, 129.5, 128.3, 127.9, 127.5, 120.9, 110.8, 60.9, 55.6, 38.5, 37.5; HRMS (ESI+, *m/z*): calculated for $C_{16}H_{17}ClO_2Na$

$[M+Na]^+$: 299.0810, found: 299.0806. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OJ column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 220 nm, retention times (min): 30.8 (minor) and 36.8 (major).



(+)-(*S*)-1-chloro-4-(1-(4-(trifluoromethyl)phenyl)allyl)benzene (2w): Purification by flash column chromatography (SiO_2, pentane) afforded a mixture of $S_N2':S_N2$ (98:2) **2w** (38 mg, yield = 45%) as a colorless oil. 84:16 er, $[\alpha]_D^{20}$ = +1.0 (c = 1 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.26 (m, 4H), 7.16 – 7.05 (m, 2H), 6.24 (ddd, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.30 (dt, *J* = 10.2, 1.3 Hz, 1H), 5.01 (dt, *J* = 17.0, 1.4 Hz, 1H), 4.77 (d, *J* = 7.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 146.8, 140.8, 139.2, 132.6, 129.9, 128.9, 128.7, 125.5, 125.5, 125.4, 125.4, 117.6, 54.0; ^{19}F NMR (400 MHz, $CDCl_3$) δ -62.4; HRMS (APCI+, *m/z*): calculated for $C_{15}H_{12}$ $[M-HClCF_3]^+$: 192.0934, found: 192.0934. Enantiomeric excess was determined by chiral HPLC analysis after hydroboration-oxidation to the corresponding terminal alcohol.



(+)-(*S*)-3-(4-chlorophenyl)-3-(4-(trifluoromethyl)phenyl)propan-1-ol (4w): Purification by flash column chromatography (SiO_2, 30% EtOAc/pentane) afforded **4w** (24 mg, yield = 48%) as a colorless oil. 84:16 er, $[\alpha]_D^{20}$ = +2.9 (c = 1 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 4.28 (t, *J* = 7.9 Hz, 1H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.48 – 2.23 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 148.1, 141.9, 132.5, 129.2, 128.8, 128.1, 125.6, 125.6, 125.5, 125.5, 60.3,

46.3, 37.7; ^{19}F NMR (400 MHz, $CDCl_3$) δ -62.42; HRMS (APCI–, *m/z*): calculated for $C_{16}H_{13}ClF_3O$ $[M\text{-}H]^-$: 313.0602, found: 313.0603. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 210 nm, retention times (min): 28.4 (major) and 30.7 (minor).

3.5 References

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